cheeked Capuchin (*Cebus lunatus*) from South America, presented by Mr. Adrian Hope, F.Z.S.; an American Red Fox (*Canis fulvus*), a Rough-legged Buzzard (*Archibuteo lagopus*) from Labrador, presented by Lord Hobart; three Vulturine Guinea Fowls (*Numida vulturina*), a Crested Guinea Fowl (*Numida cristata*) from East Africa, presented by Vice-Admiral John Corbett, C.B.; two Malabar Mynahs (*Sturnia malabarica*) from Hindostan, a Chinese Mynah (*Acridotheres cristatellus*) from China, a Waxwing (*Ampelis garrulus*), European, presented by Mr. A. F. Weiner, F.Z.S.; five Fat Dormice (*Myoxus glis*), European, presented by Mr. Edwin Liot; seven Green Tree Frogs (*Hyla arborea*), a Green Lizard (*Lacerta viridis*), three Spotted Salamanders (*Salamandra maculosa*), European, presented by the Rev. S. R. Wilkinson, F.Z.S.; an Anaconda (*Eunectes murinus*) from South America, presented by Capt. E. Ball; an Elliot's Guinea Fowl (*Numida ellioti*), a Vulturine Guinea Fowl (*Numida vulturina*), three Mitred Guinea Fowl (*Numida mitrata*) from East Africa, a Booted Eagle (*Nisaetus pennatus*), European, purchased.

ON THE GRADUAL CONVERSION OF THE BAND SPECTRUM OF NITROGEN INTO A LINE SPECTRUM

PROF. WÜLLNER, of Aachen, has recently published a treatise on the two different views which are held by physicists with regard to the various spectra presented by gases which are rendered incandescent by means of induction sparks. One of these views was first stated by Ångström, who thought that for a certain gas only one spectrum was possible, and that this spectrum consisted of lines only. All band spectra which occasionally appeared when gases were examined in the way mentioned, he ascribed to impurities. The band-spectrum of nitrogen, according to his idea, belonged to oxides of that element. He believed that as long as the current passed through the gas without giving a spark, the oxide was rendered incandescent as such, without decomposition, and that the spark decomposed the oxide, and that only then the nitrogen could give its own line-spectrum. Later on Ångström modified this view, and admitted that an elementary substance might give several spectra when rendered incandescent in the gaseous state, but he still held that in this case the element in question entered into isomeric compounds with itself, and that the different spectra belonged to different isomeric compounds. Mr. Lockyer afterwards defined this view more clearly, stating his opinion that the line-spectrum is produced by simple atoms, and the continuous or channelled-space spectra by conglomerations of molecules.

Prof. Wüllner, however, does not consider this hypothesis necessary for the explanation of the different spectra of elements, but holds that they may be explained by Kirchhoff's maxim. Prof. Zöllner has pointed out that the light emitted by a radiating layer of gas must essentially depend on the thickness and density of the layer. Prof. Wüllner, therefore, after having first confirmed the fact that the line-spectrum of elementary gases only appears with the real electric spark, the band-spectrum, however, when in the gas the electro-positive brush and glow appears, ascribes the different spectra to the differences in the radiating layers of gas. He believes that in the spark only the molecules struck by the spark are glowing, therefore almost only a linear row of molecules; thus in the spectrum only the absolute maxima of the emission power, which correspond to the temperature of the spark, become apparent. If, however, in the positive brush light the whole quantity of gas contained in the spectral tube is rendered incandescent, then it is always a relatively thick layer which emits light; in the spectrum all those kinds of light must show themselves for which at the respective temperature the power of emission is above zero. But since the incandescent gas is always of relatively small density, all the differences in the emission power of the various kinds of light must become apparent in the spectrum, and thus the latter must be richly varied or shaded; this is indeed the case in the band-spectra of gases. Prof. Wüllner adduces the spectra of iodine vapour as proofs of the correctness of his view. When rendered incandescent by means of a hydrogen flame, iodine vapour gives the negative absorption spectrum, which is of the same character as the band-spectra of gases; if rendered incandescent through the spark, the glowing iodine molecules give a bright line-spectrum.

The band-spectrum of nitrogen shows, that this element at the temperatures obtained by electric discharges possesses quite as great a power of absorption as that of iodine vapour at low temperatures, because the band-spectrum of nitrogen is essentially of the same character as that of iodine vapour, however different it may be from it in detail. Of all other gases, nitrogen must therefore be particularly adapted for showing, through the examination of the light it emits, the dependence of spectral phenomena from the thickness and density of the radiating layer of gas, and thus for furnishing the proof that there is no constant spectrum of nitrogen, but that a certain spectrum exists only at a certain temperature and density of the gas. This indeed is the question upon which turns the difference of opinions of Ångström and Lockyer on the one hand and of Wüllner and Zöllner on the other; the former ascribing the different spectra to chemical differences in the molecular conditions of the gas, the latter merely to differences of temperature, density, and thickness of the radiating layer.

In a former treatise on the nitrogen spectrum, Prof. Wüllner, without having recognised the importance of the density of the radiating layer with regard to the light emitted, pointed out that when the pressure in a nitrogen tube is diminished to such an extent that it ceases to be measurable, the brightness of the spectrum decreases, and in such a manner that the darker parts first fade away, so that at last only the brightest parts remain. He added that in this way the nitrogen spectrum in its character approaches a spectrum of the second order (the name given to line spectra by Plücker) without, however, changing to the nitrogen spectrum of the second order, since no new bright lines appear. At that time, however, Prof. Wüllner did not continue his researches in that direction, and in particular he did not examine whether the bright parts remaining do indeed correspond to the maxima of the complete band spectrum, because the spectra he obtained at those pressures were too weak to allow of measurements being made with the instruments then at his disposal. Lately, however, the Professor has minutely examined the nitrogen spectrum in this sense, employing a simple contrivance for rendering the spectra bright enough for measurements, even at the lowest pressures. This consisted in the employment of spectral tubes of very narrow calibre (about 2 mm. in diameter).

It must be remembered here that the temperature of the gas, which is caused by the induction current, rises with decreasing diameter of the tube. (If, however, the tubes were taken too narrow, the current at once broke them.)

Since the resistance in the tube rises as the density of the gas decreases, at least from a certain point of low pressure downwards, the temperature rises as well. If the rise in the temperature was sufficiently great, the experiment described by Prof. Wüllner necessarily decided the only hypothetical part in his conception of spectral phenomena, viz., whether with a rising temperature the absorption power for the various kinds of light grows in a similar manner or not. If it does grow simultaneously with the temperature, then the relative maxima of intensity of light which the complete band spectrum shows must always remain the same; the bright parts remaining at the lowest density must correspond to the maxima of the band-spectrum. If the contrary is the case, and this is what Prof. Wüllner assumes, then dark parts in the band-spectrum may become the brighter ones as the density decreases, and the bright parts remaining at the lowest pressure may be situated at places in the spectrum differing widely from the maxima of the band-spectrum. The first part of the experiment therefore consisted in an exact determination of the relative maxima in the band-spectrum of nitrogen for the sake of comparison. This is minutely described in Prof. Wüllner's paper. The final results of the observations were in complete accordance with the Professor's conception of the spectral phenomena. There is indeed no definite nitrogen spectrum when in layers of sufficient thinness the density of the gas is reduced below a certain limit. The band spectrum changes step by step into a line-spectrum; this, however, is not identical with the line-spectrum produced by the spark, but has only a certain number of lines in common with it. In this gradual change it is easy to follow the displacement of the maxima of brightness which takes place little by little as the temperature rises, and is quite conspicuous in several places; this displacement is the very cause why in this line-spectrum the lines in places differ widely in their situation from the maxima of brightness of the band spectrum.

Prof. Wüllner then gives an exact description of that part of

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the complete band-spectrum (at a pressure of about 5–10 mm.) in which the variability of the spectrum is most conspicuous, viz., in the green and blue (from wave-lengths 562 to 449); this is followed by an account of the gradual changes taking place in two different places when the density of the gas is decreased. It would lead us too far to enter into the details here; suffice it to say that the richly-shaded band-spectrum changes quite gradually into a line-spectrum, and that most of the lines of the latter are in places which show no maximum of brightness in the band-spectrum. It results from these observations that the positions of the maxima of emission-power do not remain at all the same in all temperatures, but that in consequence of the changes of temperature accompanying the decrease of pressure they may be considerably displaced.

Prof. Wüllner gives the reasons why the wider tubes are unsuitable for the gradual conversion of band-spectrum into line-spectrum, and eventually describes the differences between the line-spectrum obtained from the band-spectrum in the manner described, and the line-spectrum obtained by the spark. Upon comparison of those regions in the two spectra which were examined more closely (beginning at wave-length 572), it was found that in the spark-spectrum there are about forty lines in this region. Of these eight correspond very closely to maxima or lines in the fully developed band-spectrum. The number of coincidences with the lines of the low density line spectrum is, however, much greater; perfect, or very nearly perfect coincidence occurs in nineteen lines, *i.e.*, about half the number, and amongst these there are four which are the same in the three different forms of the nitrogen spectrum. The brightest lines of both line-spectra are, indeed, perfectly coincident. These are the yellowish-green lines 568,4 and 567,1, the green lines 500·7 and 500·4 (which result from the green-channelling described in detail) and the blue line 463·2 (developed from the blue channelling). Another interesting similarity exists between the two line-spectra, however differently about half of their lines may be situated.

Plücker and Hittorf distinguish five principal groups in the line-spectrum of nitrogen, between which there are other single lines. Of these five groups Nos. II. to V. belong to the region specially studied by Prof. Wüllner. These groups are:—

Group II. between wave-lengths 577—567
Group III. ,, ,, 555—545

Between groups III. and IV. there are first three lines: 535·6, 534·4, and 532·3; and then two lines: 518·1, and 517·6.

Group IV. between wave-lengths 508—499

Between groups IV. and V. there are first four lines: from 489·6, to 484·8, and further on three lines: 480·5, 479·0, and 478·1.

Group V. between wave-lengths 464·5—460·2.

All these groups are situated in such parts of the spectrum where also the line-spectrum developed from the band-spectrum is very rich in lines. It follows, therefore, that the spark-line spectrum is developed, on the whole, in such places which show the greatest variability, even in a gradual decrease of the density of the gas, and which are richest in lines in the low-density line-spectrum.

Prof. Wüllner recapitulates his interesting treatise in the following manner:—The course of spectral phenomena of nitrogen, which takes place when the gas is gradually reduced in density in tubes of sufficiently small diameter, shows exactly those changes which may be deduced from Kirchhoff's maxim, that the smaller the number of incandescent molecules, the more the spectrum contracts into a number of bright lines.

At the same time it may be directly observed when the density of the gas is decreasing, how, in consequence of the temperature rising through increasing resistance in the tube, the maxima of brightness change their position, how the maxima of the fully-developed band-spectrum fade away, and how the lines become prominent in places which are either secondary or tertiary maxima or uniformly illuminated regions in channelled spaces. Now, if we further consider that the lines of the spark-spectrum, compared to those of the former line-spectrum, are not more considerably displaced than the latter are with regard to the maxima of the band-spectrum, then we can hardly doubt that in the different forms of the nitrogen-spectrum we see nothing else but the light emitted each time in accordance with the different temperature, density, and thickness of the radiating layer of gas, and that a new hypothesis for the explanation of these spectral phenomena is unnecessary and superfluous.

A HISTORICAL SKETCH OF THE VARIOUS VAPOUR-DENSITY METHODS[1]

ALTHOUGH Southern,[2] in 1803, made some very careful experiments to determine how much water was required to furnish 1 cubic foot of steam at various pressures, still the foundation of vapour-density methods was laid by Gay-Lussac.

He, in 1811,[3] started on the correct basis of accurate work when he heated a weighed quantity of substance over mercury in a graduated vessel. Muncke, in 1816,[4] heated the substances *in vacuo* in elliptic glass balloons of 155 c. i. capacity, closed with a stop-cock and with thermometer and syphon barometer suspended inside. In 1822[5] Cagniard de la Tour determined the combined effects of heat and pressure on certain volatile liquids, but as his results were on the question of maximum vapour-density, they hardly enter the domain of the present sketch. In the same year Despretz,[6] who gave no drawing, and only a very imperfect description of his apparatus, published a method in which he used a 9-litre exhausted globe, and made his determinations at atmospheric temperatures, employing only a small quantity of substance.

In 1826 Dumas,[7] wishing to operate on substances which attack mercury, worked out and published his well-known method in which the volume is definite, but the amount of substance required to fill that volume with vapour has to be subsequently determined.

In 1833[8] Mitscherlich proposed using tubes, sealed at one end and drawn to a neck at the other, instead of bulbs, and gave details and drawings of the apparatus for heating them; but Dumas, two years later, objected to the proposed alteration in his method, for he wrote:—

"We must then leave to this operation all its simplicity to make it essentially practical, and such, in fact, that with an ordinary cast-iron pot and some pieces of iron wire we can perform it. This is what I have done from the first, and what I persist in doing, my aim never having been to make a piece of apparatus for the cupboard of the physicist, but to give chemists a simple and eminently practical and yet exact process. After all *they* are the only ones to be considered."[9]

Deville and Troost,[10] however, in 1860, in referring to that same apparatus, called it "La méthode si élégante de M. Mitscherlich."

Bineau, in 1838,[11] published an elaborate paper, but unfortunately without any drawings, for when we read the following paragraph, "The bodies on which I have worked have been volatilised sometimes by the aid of heat by following the process of Dumas or that of Gay-Lussac, sometimes without elevation of temperature by working in the barometric vacuum or by allowing the vaporisation to take place in dry air or hydrogen," we cannot but feel that an enormous amount of valuable work has been lost for want of details. In 1844 we find Cahours,[12] as well as Bineau,[13] at work at the same subject. In 1846 the latter[14] repeated the experiments of Despretz with slight modifications, but called attention to the fact that the result was seriously affected by very small errors in reading off the mercurial column.

In 1849 Regnault[15] described an apparatus very similar to that of Mitscherlich, but arranged the tube supports so that the two could be withdrawn simultaneously; he also dispensed with sealing the tube containing air by providing it with a stop-cock. Bineau,[16] in 1859, in order to operate at high temperatures, coated the glass tubes with clay and heated them in a sand-bath.

Regnault,[17] in 1861, to obtain the same result, used iron tubes, and to ensure uniformity of temperature, heated them in a cast-iron tube which was made to revolve over gas-burners. The tube which served as air-thermometer was furnished with a stop-cock, but that containing the substance only terminated in a small aperture, and was not closed, as a sufficient quantity was

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[1] Paper read at the British Association by Jas. T. Brown, F.C.S.
[2] *Phil. Mag.*, 30, 113 (1847).
[3] *Ann. de Chim.*, 80, 218 (1811); *Gilbert Annal.*, 45, 332 (1813).
[4] *Schweigger's Journ. Chem. Phys.*, 22, 1 (1818).
[5] *Ann. Chim. Phys.*, 21, 127 and 178 (1822); 22, 410 (1823).
[6] *Ibid.*, 21, 143 (1822); *Quart. Journ. Sci.*, 15, 297 (1823).
[7] *Ann. Chim. Phys.*, 33, 337.
[8] *Ibid.*, 55, 5–41 (1833).
[9] "Traité de Chimie," 5, 44.
[10] *Ann. Chim. Phys.* [3], 58, 259.
[11] *Ibid.*, 68, 416.
[12] *Compt. Rend.*, 19, 771 (1844); *Pogg. Annal.*, 63, 593 (1844).
[13] *Compt. Rend.*, 19, 768 (1844); *Liebig's Ann.*, 65, 424 (1845).
[14] *Compt. Rend.*, 23, 414 (1846); *Ann. Chim. Phys.*, 18, 226 (1846); *Ann. Chem. Pharm.*, 60, 158 (1846).
[15] "Cours de Chimie," 4, 66 (1849).
[16] *Compt. Rend.*, 49, 799 (1859).
[17] *Ann. Chim. Phys.* [3], 63, 54 (1861).

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